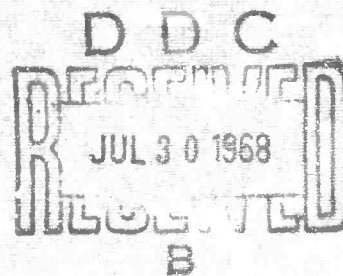


Anodic Oxidation of Hydrogen on Iron and Platinum in Sodium Hydroxide Solution

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May 24, 1968



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AD 672314

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ABSTRACT

In a rigorously controlled high-purity closed system, the electrochemical behavior of Fe and Pt electrodes for the hydrogen oxidation reaction showed marked differences in both the active and passive regions. The catalytic behavior of the two metals reflects the differences in metallic properties and anion adsorption. Iron was found to be a far better catalyst with a much less pronounced passive region. Iron corrosion was insignificant. Small amounts of platinum on iron strongly retarded hydrogen oxidation. Significant Pt dissolution and deposition on the iron working electrode was not found.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem M04-08
ARPA Order 878

Manuscript submitted March 20, 1968.

ANODIC OXIDATION OF HYDROGEN ON IRON AND PLATINUM IN SODIUM HYDROXIDE SOLUTION

INTRODUCTION

Recent work at NRL (1,2) has indicated that the passivation of the hydrogen oxidation reaction on platinum in acid solution is caused by anion adsorption. (Passivation is herein defined (2) as the anodic region in which $dE/d(\log i)$ is negative.) Anion adsorption initially caused rather moderate passivation effects due to the blocking of active sites in such a way as to cause a reduction in the effective electrode area. The major passivation effect, however, was due to a poisoning of catalytically active sites with strongly adsorbed anions and, under proper conditions, a combination of desorbed oxygen atoms and adsorbed anions.

The present work was undertaken to relate these findings to both Pt and Fe electrodes in alkaline solution. In addition, the question was considered of the effects that trace amounts of platinum deposited on pure iron in alkaline solutions would have on the behavior of the iron. This is an important question inasmuch as Pt counter and reference electrodes are commonly used in such experimental studies. Malachuk et al. (3) have indicated that anodic polarization of platinum in alkaline solutions can cause deposition of platinum on the working electrode.

EXPERIMENTAL

The high-purity closed electrochemical system and experimental conditions were the same as previously reported (1,4) with the exception that the solution was 0.2M NaOH. The working electrodes were a Pt wire (99.99%, 20-mil dia., geometric area = 0.65 cm^2), an Fe wire (fabricated from three-pass-electron-beam zone-refined iron with less than 4 ppm total metallic impurities, 20-mil dia., geometric area = 0.65 cm^2), and a similar Fe wire with about 1 cm of 3-mil Pt wire spot-welded to the Fe wire and wound around its tip (Fe \gg Pt electrode). Each of these electrodes was connected to Pt leads and sealed off in lead-free soft glass tubes. The counter electrode was a large Pt gauze electrode. The reference electrodes were in an arm off the main cell compartment and were a calibrated miniature glass electrode and a Pd wire charged with hydrogen to a potential of about 50 mv positive to a hydrogen electrode in the same solution. This Pd-H wire electrode was used as the potentiostatic reference.

After the cell was cleaned with hot concentrated nitric acid it was rinsed for at least 24 hours by continually distilling triple-distilled water into it. About 100 ml of water was then distilled into the cell and cooled. A capsule of sodium metal (99.95% with <55 ppm heavy metals sealed under argon) was broken in two and introduced into the cell under an atmosphere of purified helium. The two halves of the capsule were placed so the open ends were at the bottom of the cell. Thus as sodium metal dissolved, the hydrogen gas generated filled the capsule ends and regulated the introduction of water into the capsule. This allowed a rather slow solution of sodium metal. The resulting sodium hydroxide solution was 0.2 M.

Note: This research was supported by the Advanced Research Projects Agency of the Department of Defense as part of the ARPA Coupling Program on Stress-Corrosion Cracking (ARPA Order 878).

Before the Fe electrode was introduced into the cell, a Pt wire cathode was used with the Pt gauze electrode as an anode, and the solution was pre-electrolyzed at about 50 ma for several days under a pure helium atmosphere. Upon completion of the pre-electrolysis, the pre-electrolysis cathode was removed, and the helium flow was replaced with hydrogen (purified by passing through heated Pd-Ag tubes). The potentials of the Pt wire, Pt gauze, and Pd wire were then determined against the glass electrode. After the Pt/H₂ electrodes reached their equilibrium values and the Pd wire was 50 mv positive to the Pt/H₂ potentials, the Fe wire (cleaned in 1M H₂SO₄ and rinsed with triply distilled water) was introduced into the cell and was made the working electrode. After the open circuit potential was determined, the gauze Pt electrode as the counter electrode and the Pd wire as the reference electrode were connected into the potentiostatic circuit. The glass reference electrode continuously monitored the potential on the Fe working electrode via a Keithley 610B electrometer. Current flow under potentiostatic conditions was determined with a Keithley 601 electrometer and recorded. Potentiostatic current-voltage curves were then determined after steady-state currents were achieved. Numerous runs under increasing and decreasing potential sequences were determined until reproducible results were obtained.

Similar measurements were made for a pure Pt wire working electrode. Another series of measurements was made with the Fe wire with the small amount of attached Pt wire (Fe >> Pt electrode).

While the electrodes were being held at a constant potential, the hydrogen (P_{H₂} = 1 atm) flow was about 40 ml/min. When steady-state currents were obtained the hydrogen flow rate was increased to >1000 ml/min in order to minimize diffusion-controlled reaction rates. The currents shown in the figures were determined under these conditions. The temperature was 25 ± 2°C. All potentials were converted to the normal hydrogen electrode (N. H. E.) scale.

EXPERIMENTAL RESULTS

The open circuit potential for the Pt, Fe, and Fe >> Pt electrodes were each the equilibrium potential of -0.78 v for the H₂O/H₂ reaction in the 13.2-pH, 0.2M NaOH solution. There was no visible sign of corrosion on the pure Fe wire even though the electrode was exposed for several weeks. However, the Fe >> Pt electrode did show a very small amount of a yellowish brown corrosion product in the vicinity of the platinum. Tests for iron in solution (thiocyanate) were always negative.

The steady-state potentiostatic current-voltage curves for the three working electrodes are shown in Figs. 1, 2, and 3. In each case there was some hysteresis on the decreasing potential sequence as compared to the increasing potential sequence. All of the electrodes showed Tafel regions at low anodic potentials where the rate of hydrogen oxidation was increased as the potential became more noble. At about -0.2 v for the Pt electrode (Fig. 1) there was a sharp passivation and a large drop in hydrogen oxidation rate until a potential of about 0.3 v was reached. This was followed by a limiting current density of about 3×10^{-6} amp/cm² and at 0.8 v by a Tafel region (b = 0.06 slope) at which the predominant reaction is the oxidation of water to oxygen. The hysteresis for the decreasing potential sequence is most likely caused by dermisorbed oxygen (1,4) until a potential of -0.3 v, where the hysteresis effect vanishes.

Figure 2 shows that the potentiostatic current-voltage relation for iron is very different from that of platinum. The transition to a passive state is not as sharp, and the retardation of the hydrogen oxidation reaction in the passive region is rather moderate. An O₂ formation region is reached at about 0.9 v. The hysteresis on the decreasing potential sequence may be due to either dermisorbed oxygen or an invisible layer of oxide. In any case, as the potential reaches about 0.2 v of the equilibrium value the hysteresis

Fig. 1 - Potentiostatic anodic current density vs potential on the Pt electrode

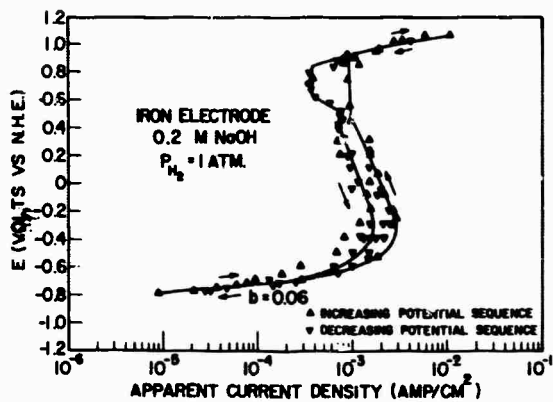
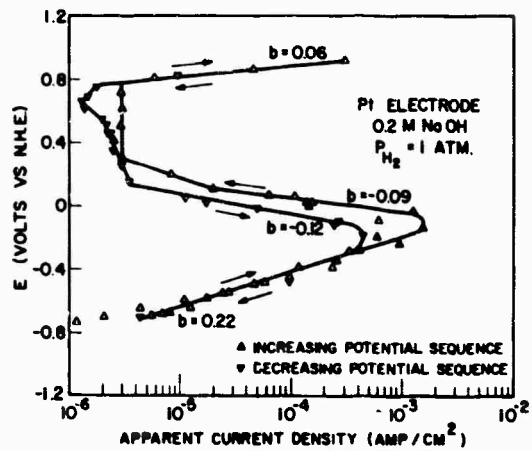


Fig. 2 - Potentiostatic anodic current density vs potential on the Fe electrode

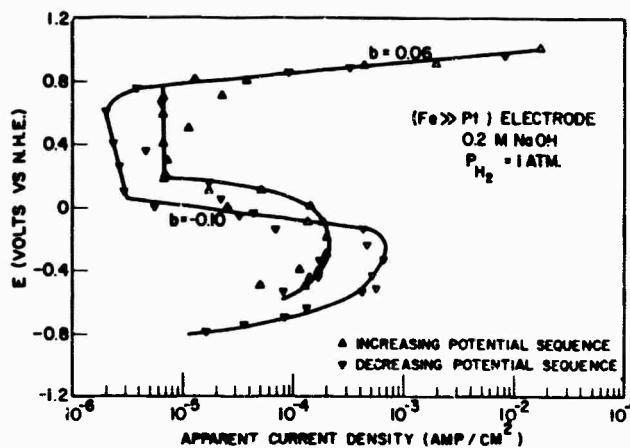


Fig. 3 - Potentiostatic anodic current density vs potential on the Fe >> Pt electrode

becomes insignificant, and the state of the iron surface is essentially the same as for the increasing potential sequence.

The data for the $\text{Fe} \gg \text{Pt}$ electrode shown in Fig. 3 indicate that the very small relative area of platinum played a dominant role. The similarity to pure iron is evident at low potentials only.

DISCUSSION

The most striking feature of the potentiostatic current-voltage relations comparing pure iron with platinum is the fact that iron is a far more active electrode for the hydrogen oxidation reaction at all potentials. Figures 4 and 5 show a comparison of the potentiostatic curves for the three working electrodes for increasing and decreasing potential sequences, respectively.

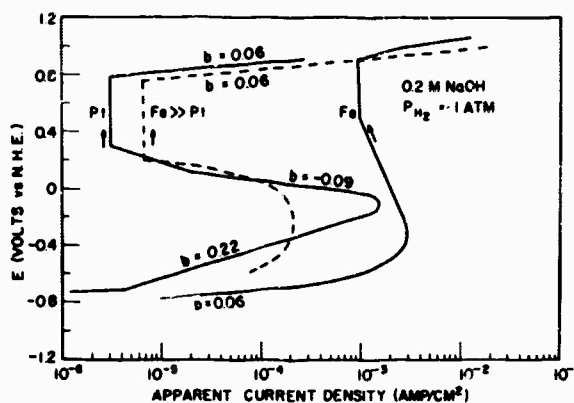


Fig. 4 - Comparison of the Pt, Fe, and $\text{Fe} \gg \text{Pt}$ electrodes for the increasing potential sequence

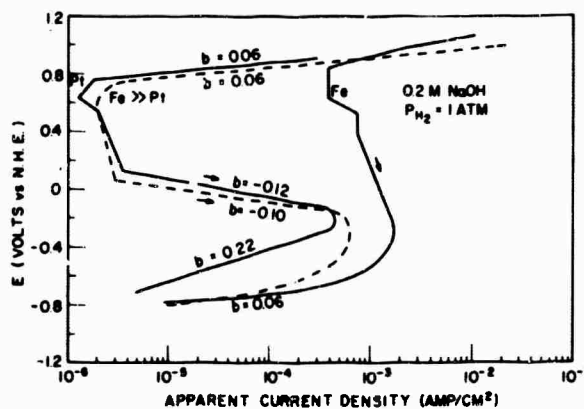


Fig. 5 - Comparison of the Pt, Fe, and $\text{Fe} \gg \text{Pt}$ electrodes for the decreasing potential sequence

The effect of a small area of Pt on the Fe wire was to decrease its activity so that it behaved more like a Pt than an Fe electrode. At low polarizations, however, the Fe \gg Pt electrode behaved more like the pure iron, especially in the decreasing potential sequence. The reduction in the limiting current density compared to both the Fe and Pt electrodes is surprising, but probably reflects the small amount of iron corrosion product formed near the Fe/Pt interface. It is evident from these experiments that trace amounts of platinum would have a marked effect on the electrode behavior of pure iron. It is evident also that, under the experimental conditions using the high-purity system, dissolution of platinum from electrodes during pre-electrolysis or during a run and the subsequent deposition of part of this Pt on the Fe electrode must have been insignificant. There is, in fact, no evidence of platinum impurity affecting the results on the pure iron working electrode. Similarly there is no evidence of traces of iron in solution depositing on the platinum working electrode and affecting its behavior significantly.

The sharpness of the onset of passivity on the Pt electrode and the almost three orders of magnitude drop in hydrogen oxidation rate in this passive region (-0.1 v to 0.3 v) indicate that the passivation is due primarily to the increase in the free energy of activation of the hydrogen oxidation reaction. This effect is most likely due to the poisoning of catalytically active sites by anion (OH^-) adsorption (2). The increase in activity in the potential range from about 0.1 v to 0.0 v for the decreasing potential sequence verifies this interpretation and, as in acid solution, shows the increased poisoning effect due to chemisorbed oxygen (2). These results are similar to those found for hydrogen oxidation passivation on platinum in sulfuric acid solution (1,2) except that the alkaline solution results are more pronounced. This is evidently due to the higher heat of adsorption of OH^- over SO_4^- ions. The much steeper Tafel slope ($b = 0.22$) shown in Fig. 1, compared to the sulfuric acid result ($b = 0.025$), reflects the fact that the rate-controlling step in alkaline solution is much more sensitive to polarization than in the acid. The 0.025 Tafel slope can be interpreted as a slow hydrogen dissociation to H_{ad} atoms, whereas the $b = 0.22$ slope indicates that the rate is due to a complex hydrogen discharge. The hydrogen discharge must be affected by the sodium ions (5). The passivation as the potential becomes more noble indicates that the influence of adsorbed OH^- ions is probably not felt until the onset of passivity.

The surprisingly moderate passivation of the Fe electrode (Fig. 2) indicates that any anion adsorption or other effects at the passivation potential did not cause a poisoning of catalytically active sites and that the retardation of the hydrogen oxidation was due primarily to a reduction in the active area (2) due to either weak anion adsorption or the formation of iron complexes with OH^- or other oxygen species. We do not, of course, know definitely that the Fe electrode is free of oxide even at the open circuit potential. However, the fact that it acts like a reversible hydrogen electrode and its low polarization eliminate the possibility of a high-resistance oxide. Indeed, it is quite feasible that in the presence of hydrogen the iron is virtually free of oxides or oxygen species. The hydrogen equilibrium potential indicates an oxide-free metal, and the Tafel slope of 0.06 is likely due to a slow hydrogen-discharge-controlled step. Additional work, however, is required to verify the state of the iron surface, both at the hydrogen equilibrium potential and under anodic polarization.

CONCLUSIONS

This work has shown that the behavior of pure Pt and Fe electrodes under the rigorously controlled high-purity closed system environment is markedly different in both the active and passive hydrogen oxidation regions. The differences in catalytic behavior of the two metals are great, and their passivation behavior strongly reflects the differences in metallic properties and the influence of anion adsorption. No significant corrosion of iron was found, and iron was found to be a far better catalyst for the hydrogen oxidation reaction at all anodic potentials. Despite this, anion poisoning of catalytically

active sites on iron was much less pronounced than on platinum. This means that anion adsorption has less effect on the surface states of iron than on platinum. Further work is required to better define the iron surface under the experimental conditions used so that its remarkable catalytic properties are understood. Under the conditions used, significant electrochemical effects due to dissolution and deposition of iron or platinum on each other were not found.

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
Naval Research Laboratory Washington, D. C. 20390		Unclassified	
3. REPORT TITLE		2b. GROUP	
ANODIC OXIDATION OF HYDROGEN ON IRON AND PLATINUM IN SODIUM HYDROXIDE SOLUTION			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
An interim report; work on the problem is continuing.			
5. AUTHOR(S) (First name, middle initial, last name)			
Sigmund Schuldiner and Clarence M. Shepherd			
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS	
May 24, 1968	10	5	
8a. CONTRACT OR GRANT NO.	8b. ORIGINATOR'S REPORT NUMBER(S)		
NRL Problem M04-08	NRL Report 6718		
b. PROJECT NO.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
ARPA Order 878			
c.			
d.			
10. DISTRIBUTION STATEMENT			
This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		Department of Defense, Advanced Research Projects Agency, Washington, D. C. 20360	
13. ABSTRACT			
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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fuel cells Corrosion Passivity Platinum Iron Hydrogen Hydrogen-oxidation Electrode reactions						